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Immobilized graphene-based composite from asphalt: Facile synthesis and application in water purification

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HIGHLIGHTS

GRAPHICAL ABSTRACT

- Facile strategy to make graphenic materials from cheaper precursor such as asphalt.
- Material can be made in solution; also as anchored on solid substrates.
- The synthesized material, GSC, was found to be excellent for water purification.
- The applicability was demonstrated through batch and laboratory columns experiments.
- The capacity was compared to other similar adsorbents and was found to be superior.

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ABSTRACT

An in situ strategy for the preparation of graphene immobilized on sand using asphalt, a cheap carbon precursor is presented. The as-synthesized material was characterized in detail using various spectroscopic and microscopic techniques. The presence of G and D bands at 1578 cm⁻¹ and 1345 cm⁻¹ in Raman spectroscopy and the 2D sheet-like structure with wrinkles in transmission electron microscopy confirmed the formation of graphenic materials. In view of the potential applicability of supported graphenic materials in environmental application, the as-synthesized material was tested for purifying water. Removal of a dye (rhodamine-6G) and a pesticide (chlorpyrifos), two of the important types of pollutants of concern in water, were investigated in this study. Adsorption studies were conducted in batch mode as a function of time, particle size, and adsorbent dose. The continuous mode experiments were conducted in multiple cycles and they confirmed that the material can be used for water purification applications. The adsorption efficacy of the present adsorbent system was compared to other reported similar adsorbent systems and the results illustrated that the present materials are superior. The adsorbents were analyzed for post treatment and their reusability was evaluated.

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1. Introduction

Graphene, a 2D sheet made up of extended carbon network, or their chemical analogs are promising adsorbents [1–7] and have great potential in water purification due to their unique physical and chemical properties including high surface area [8], antibacterial properties [9,10] and lesser cytotoxicity compared to carbon nanotubes [11,12]. However, the immediate use of graphenic materials for down-to-earth applications such as water purification is limited mainly due to the difficulty in large-scale synthesis and post treatment-handling, including solid–liquid separation [6,13].

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Discovery of chemical routes to produce graphenic materials by the oxidation of graphite to graphite oxide (GO) [14] and subsequent reduction to reduced graphene oxide (RGO), closely resembling graphene with extended double bonded sp² carbon network with edge carboxylic acid moieties [15-19] opened up the pathway for mass production of RGO. Recently, we have shown that RGO and chemically reduced graphene can be bound on cheap substrate such as river sand and such substrates are effective in contaminant removal [6]. In another effort, Gao and coworkers have demonstrated that GO-coated sand, termed as 'super sand', could be used as a low-cost water purification material for the developing economies [20]. The use of GO/RGO supported on silica as adsorbent for solid phase extraction was also reported recently [13]. These materials got wide publicity in the world news due to their likely utility in water purification. These composites were prepared through two-step processes that involve the preparation of graphene through relatively laborious chemical conversion of graphite to graphite oxide [14,21] and subsequent reduction of GO by hydrazine to RGO [15]. In the second step, the GO/RGO was immobilized onto sand via heat treatment [20] or by directly binding them covalently onto silica [13] or by using molecular binders [6]. However, the preparation of RGO involves the use of a variety of chemicals including hydrazine, P₂O₅ and K₂S₂O₈ which produces undesirable hazardous products like, P₂O₃, SO₂, etc. This necessitates laborious steps including post-synthesis cleaning. Developing an efficient and eco-friendly graphenic adsorbent generated from a cheaper source is desirable for water purification. Several graphene based composites with metals and metal oxides have also been demonstrated to be useful for this application. As cost is an important criterion in the success of such materials, new approaches for their production are necessary. Efforts have been made to grow graphene from diverse sources. Recent studies show that graphenic material can be synthesized from cheaper sources of carbon, like sugar [7,22] using a modified CVD process [23]. Graphene was also prepared from food, insects, and waste using a similar methodology [24]. This is necessary as chemically different carbon sources are available in different parts of the world. Among these, asphalt and various petroleum products are important to consider. A simple synthetic route is always preferable when it comes to applications such as water purification, where the use of chemicals should be avoided as much as possible.

Here, a method for the in situ preparation of graphenic material anchored on a solid substrate starting from a cheap and locally available material, asphalt, is discussed. A single-step strategy was used to immobilize the graphenic material on sand surface. Application of the as-synthesized material as a water purifying medium is reported using a pesticide and a dye as examples. Synthetic dyes mostly being non-biodegradable can have acute effects on exposed organisms and aquatic life. Exposure to such dyes can cause abnormal coloration and resultant reduction in photosynthetic efficiency. Pesticides, designed to induce acute effects or kill living organisms, are highly toxic to the environment and to all living forms including humans. We have used rhodamine-6G (R6G), a rhodamine dye and chlorpyrifos (CP), an organo-phosphorus pesticide in our studies. The adsorption capacity of the reported adsorbent was compared to several other adsorbents reported and the superiority of the present system is demonstrated. The simple and cost effective methodology adopted here facilitates the preparation of large-scale graphenic material and immobilization of the material on sand surface without any external chemical agents, in a single step. This may open up the practical use of graphenic materials. The solution based processability of the sample has also been demonstrated. However, additional experiments are needed to validate the applications of the material.



Scheme 1. Schematic illustration of the formation of GSC.

2. Materials and methods

Materials, in situ synthesis of graphene-sand composite (GSC), batch adsorption experiments, fixed-bed column experiments, instrumentation and the mechanism for the formation of graphene are given in supplementary data 1. The process of preparation of GSC starting from asphalt and sand is shown in Scheme 1.

3. Results and discussion

3.1. Characterization of the graphene-sand composite (GSC)

GSC was characterized using different microscopic techniques. Fig. 1A and B shows the SEM image of the prepared composite. The sheet-like structure covering the surface of the sand particles indicate the formation of graphenic material. Asphalt coated samples before heating had a sticky coating over the surface and formed aggregated clusters (insets in Fig. 1A and B). To understand the elemental composition of the material, the composite was analyzed using EDAX (Fig. 1C), where, we can see that the major elements present are carbon, silicon and oxygen. Inset in Fig. 1C shows the SEM image of a GSC particle and the corresponding elemental maps. Si and O features are due to sand (SiO₂). The large C feature points to the presence of graphenic material formed over the sand surface.

The (002) diffraction of graphite (002) appears at $\sim 26^{\circ}$ (2 θ) in CuK α powder X-ray diffraction (XRD) and as it is getting exfoliated, due to the increase in inter-layer spacing, this feature is known to occur at lower values. Fully exfoliated graphite oxide is known to show this feature around 11°. River sand, used as a substrate in this study, also showed a feature in the same region and at lower carbon contents, no feature corresponding to graphene was observed. Graphenic material formed in the study was treated with



Fig. 1. (A and B) SEM images and (C) EDAX spectrum and the corresponding elemental maps of GSC (5% loading). A higher loading was used for getting a more clear observation of the film in SEM and EDAX mapping. Insets in (A) and (B) show the corresponding asphalt coated samples before heating. Clustered particles can be seen in the expanded figure.



Fig. 2. (A) Photographs of the prepared graphenic material dispersed in toluene at different wt% of initial asphalt. (B) TEM and (C) SEM images of a graphene sheet and (D) Raman spectra taken from the sample showing the D and G band. Inset shows the XPS spectrum in the C 1s region. The TEM image shows foldings of 2 nm thickness (marked).

acid and has undergone heat treatment as well. Hence, the multilayer structures getting formed in the study are expected to have higher d-spacing compared pristine graphite. Our observations are consistent with these. A new peak was seen around 22° for GSC of 2% loading and at 24° for GSC having 5% loading. This was attributed to (002) diffraction of multilayer graphenic structures. XRD data of GSC at these two carbon loadings and a comparison with bare river sand is included in supplementary data, Fig. S2.

The possibility of producing graphenic material in dispersed phase was also investigated. The procedure employed for the preparation of GSC was carried without the presence of sand. The material obtained was suspended in N-Methyl-2-pyrrolidone (NMPs) by mild sonication, which points to the non-polar nature of the material. Hence, the presence of oxygen functionalities can be neglected [25]. This material was analyzed using microscopic and spectroscopic techniques. Fig. 2A shows the dispersibility of the material in NMP. Near perfect colloidal dispersions of the material at different weight percentages can be seen in the figure. Fig. 2B shows the TEM taken from such a sample (0.0005 wt%). We can see large sheets spread over μm^2 area. Large number of wrinkles, which characterize graphene, can be seen on the surface confirming that the material prepared is graphenic, comprising of thin sheets. However, in some areas of the grid thicker sheets were also seen. Fig. 2C shows the SEM image of such a thick film spread over μm^2 area. Hence, we can conclude that the present methodology predominantly gives multi-layer graphenic structures. The sample was analyzed using Raman and XPS as well (Fig. 2D). Raman spectrum clearly showed a prominent G band and a less intense D band at 1578 and 1345 cm⁻¹, respectively. The presence of such a peak again points to the material being graphenic in nature. The presence of D band points toward the presence of defects. We attribute these defects to structural defects other than those arising from the presence of oxygen functionalities. Moreover, most of the functionalities are unstable at 400 °C. In the present methodology, due to the presence of multilayers, a larger number of grains can be present, giving rise to the D-band observed. The 2D region had a broad feature similar to chemically prepared graphene (RGO). Presence of the D-band (and the associated D + D' band) and the presence multi-layer structure might be reducing the intensity of 2D band. To confirm the absence of oxygen functionalities, the sample was analyzed using XPS. The inset of Fig. 2D, shows the deconvoluted XPS spectrum in the carbon 1s region of the prepared material. We can clearly see that the carbon is unfunctionalized, nearly completely.

As the main theme of this work being the creation of a cheap graphenic adsorbent for water purification, the supported composite was analyzed in more detail. The material was characterized using Raman and XPS extensively. Fig. 3A shows the Raman spectra at different stages of GSC preparation. Initial sand showed a prominent feature at 470 cm^{-1} (due to SiO₂). However, upon coating with asphalt, all the features disappeared (curve ii in Fig. 3A). Only a large fluorescence background due to asphalt was seen. Upon heating the particle at 250 °C (curve iii), a small G-band started to appear. Still, the large fluorescence background was persistent. Curve iv shows the Raman spectrum of the final GSC sample. The sample clearly showed a prominent G-band centered at 1578 cm⁻¹ and a less prominent D-band at 1345 cm⁻¹ pointing to the formation of graphenic material. The peak at 470 cm⁻¹ confirmed the presence of sand. The resulting sample was compared with RGO supported on river-sand sample (RGO@RS) prepared through the methodology reported earlier [6]. Curve v shows the Raman spectra collected from RGO@RS. We can see that there are close similarities between the samples, indicating that the GSC prepared is closely related to the graphenic adsorbent in the literature [6,19]. On closer examination we can see that the intensity of the D band is much lesser in GSC, indicating the lesser extent of defects in the sample compared to RGO@RS. It is proposed that this may be due to the absence of oxygen functionalities in GSC. We can also see that the 2D region is more prominent in GSC compared to RGO@RS. Hence, it might be proposed that graphene formed in the present case is of better quality than RGO.

Panel B in Fig. 3 shows the XPS of GSC at different stages of synthesis. Fig. 3B a1 shows the survey spectrum of the asphalt coated sand sample. The C 1s region of the same sample is given in a2. We can see that the carbon is highly functionalized with several components other than the most prominent peak at 284.5 eV (a2). The survey spectra (b1 and c1) show that as the heating and acid treatment is done to the sample, most of the oxygen is getting removed from the sample. This is expected since the thermal stability of most of the functional groups is lesser than the temperature used and due to the use of strong dehydrating agent (H_2SO_4). Upon heating at 400 °C, these extra features disappeared to give a single component (b2). After acid wash also only one component was seen for C 1s (c2) showing that the carbon is mostly unfunctionalized.

Carbon loading on GSC was calculated using TGA (supplementary data Fig. S3). Pristine sand did not show any weight loss when subjected to heat treatment. However, for 2 wt% asphalt loaded sand, there was a weight loss of about 0.8% indicating the removal of functional groups in asphalt leaving behind pure carbon. Using this, the exact carbon content on GSC was calculated and different sets of composites with varying loading (wt% loading) and varying sand particle size were prepared. Fig. 4 shows the SEM images of GSC having different carbon loading. The sand particles to begin with were pretty clean and had no covering on the surface (supplementary data Fig. S4). As the loading of graphene was increased, a layer was progressively visible on the surface (details are given in supplementary data 5). Similarly, GSC with different sand particle size having the same loading was also prepared (supplementary data Fig. S6).

3.2. Batch adsorption experiments

3.2.1. Parameter optimization

In this study, the R6G removal performance of the material synthesized at various conditions were tested. The variables in



Fig. 3. (A) Raman spectra at different stages of preparation of GSC. (i) Sand, (ii) asphalt coated sand, (iii) heated at 250 °C, (iv) GSC and (v) RGO@RS. (B and C) XPS analysis of GSC at different stages. a1, b1 and c1 are the survey spectra and a2, b2, and c2 are the corresponding C 1s spectra: (a1 and a2) asphalt coated sand, (b1 and b2) asphalt coated sand particles heated at 400 °C before acid wash and (c1 and c2) after acid wash (GSC).



Fig. 4. SEM images (larger and small area) of GSC having different carbon loading (A and B) 0.2, (C and D) 0.5 and (E and F) 1 wt% of graphenic carbon. (G) Photographs of pristine sand, sand coated asphalt and GSC of different loading.

synthesis were carbon loading, particle size and process temperature. Fig. 5A shows a direct correlation between the carbon content and adsorption capacity. The maximum uptake was observed at a loading of 1 wt% and further loading did not affect the adsorption capacity greatly. The plausible reason might be that, as the loading increases from 0.2 to 1 wt%, sand surface is progressively getting covered by graphene resulting in large increase in the effective surface area and at 1 wt%, a complete coverage occurs. Upon further increase in loading, only multi-layers are getting formed which do not increase the effective surface area significantly. Hence, no appreciable increase in uptake capacity was observed further.

The effect of sand particle size on the adsorption capacity was also tested (Fig. 5B). As expected, the data show an increase in the uptake with decrease in sand size due to the increase in effective surface area. The synthesis temperature was also optimized through several iterations and the optimum performance was achieved at 400 °C. The auto-ignition temperature of the material is above 400 °C, so further increase in temperature beyond 400 °C in the presence of oxygen was not possible. The temperature was increased to 500 °C under nitrogen atmosphere but it did not show any appreciable increase in graphene quality or adsorption efficiency. Fig. 5C shows the effect of heat treatment as a function of time. The data show an optimum heating time of 4 h and further heating did not change the uptake much. The adsorbent dose was also optimized as a function of pollutant uptake. The percentage capacities increased with increasing dose. This can be attributed to increase in adsorption sites with increasing dose. 100% removal efficiency (for the used pollutant concentration) was observed with an adsorbent dose above 50 g/L (Fig. 5D). With acid treatment, the adsorption capacity of the sample increases significantly (about 12%, supplementary data S7) possibly due to increase in the number of adsorption sites of the composite or due to some electrostatic interaction between GSC and the pollutant [27]. Our recent ab initio calculations have shown that adsorption is likely to be mediated by adsorbed water itself [28]. Still the adsorption mechanism is unclear as far as graphene is concerned.

The CP removal capacity of the adsorbent was also tested. CP had a prominent adsorption peak at 297 nm in the UV/vis spectrum. The change in the spectrum during exposure is shown in Fig. 6A. The kinetics was observed to be faster for the initial stages (up to 120 min) but then slows down significantly. Complete removal (below the detection limit) of CP was assumed when no peak was



Fig. 5. Effect on adsorption capacity of the composite with change in (A) carbon loading, (B) sand size, (C) heating time and (D) adsorbent dose. The capacity is manifested in terms of the decrease in the absorbance of R6G upon exposure to GSC after an exposure of 1 h.

observed at 297 nm. About 250 mg of GSC (0.5 wt%) removes 4 ppm of CP (10 mL) completely.

The versatility of the adsorbent in removing pollutants/colored materials was further explored with the experiments conducted with Coca-cola. The original Coca-cola after dilution with water (1:20) has an adsorption peak at 274 nm. The decrease in peak height with respect to time confirms that GSC can decolorize Coca-cola as shown in Fig. 6B. Column experiments were also done to confirm the results (supplementary data video1 in S8). It was seen that the adsorption is very fast and 50 cm column of 8 cm length filled with GSC of 1% loading efficiently decolorized 200 mL Coca-cola in 20 min.

3.2.2. Kinetic study

Adsorption rate is an important parameter in designing batch or continuous adsorption process. The pollutant removal was tested as a function of time and the data are shown in Fig. 7. Here, we used R6G as the model pollutant (10 mL) and 500 mg of 1 wt% (loading) of GSC as the adsorbent. As we can see, the kinetic data exhibited rapid removal of R6G. More than 65% of the pollutant was removed in the first 60 min and the system reached pseudo equilibrium in 240 min and further contact did not make noticeable change in the uptake. Control samples were also run to account for any possible natural attenuation and the data showed insignificant effect. Estimation of adsorption rate constants was done by fitting the experimental data with well-known adsorption kinetic models, viz. Langergren pseudo first-order kinetic model [29], and Ho's pseudo-second-order kinetic model are given in supplementary data 9. The inset in Fig. 7 shows the pseudo first and second order model fitted data along with experimental data. The data analysis and associated error measurements show that pseudo second-order model is more appropriate to describe the system and the data fitted well with more than 99% confidence level.

3.3. Fixed-bed column experiment

Laboratory based fixed bed adsorption studies are important in order to obtain basic engineering data for the design of any



Fig. 6. (A and B) Adsorption experiments using GSC. The adsorbents were CP and Coca-cola, respectively for A and B. A standard Coca-cola sample was diluted 20 times with deionized water.



Fig. 7. UV/vis data showing time dependant removal of R6G. The inset shows the removal of R6G as function of time (primary axis). The pseudo and second order model fits are shown in secondary axis. Initial R6G concentration = 1/mg/L; flow rate = 2.3 mL/min.

adsorption column. In this study, removal of R6G from contaminated water using columns packed with GSC was examined. The ratio of column diameter to the diameter of the particles was approximately 100, which is much above the ratio reported to overcome the premature leakage with wall effect [33,34]. Three successive cycles of adsorption and desorption were carried out in situ to test the reusability. After the first adsorption cycle, the bed was regenerated in situ by backwashing with 42 bed volume of acetone at flow rate of 2.3 mL/min followed by purging with hot air to remove the entrapped/adsorbed acetone. Fig. 8A shows the adsorption and desorption breakthrough curves and the data are summarized in Table 1. From the data it is clear that the material can be used in multiple cycles without affecting the adsorption capacity significantly. The reduction in adsorption was found to be less than 5% at the end of the third cycle (Fig. 8B).

3.4. Comparison study

The superiority of our material over other similar absorbents was investigated. We compared the adsorption capacity (q) of the

Table 1

Breakthrough parameters obtained during three consecutive cycles of adsorption.

Cycle number	Bed height (cm)	Breakthrough volume (mL)	Adsorption capacity (mg/g) of carbon
1	3	3547	44.5
2	3	3260	42.3
3	3	3146	40.4

as-synthesized material with RGO@RS, GSC750, GOSAND (also called super-sand). While the performance of RGO@RS and GSC750 was evaluated in the lab; that of GO_{SAND} was taken from the literature [20]. RGO@RS was prepared as reported by Sreeprasad et al. [6] and GSC₇₅₀ was prepared from sugar [7], where carbon loading was fixed as 0.5 wt% in both cases. A comparison of *q* of GSC, GSC₇₅₀. and RGO@RS was made based on batch experiments. 100 mg of sand-composites having 0.5 wt% of carbon content were taken separately and their adsorption efficiencies were evaluated with 10 mL of 5 ppm R6G. The adsorption experiment was performed as mentioned previously and the sample was allowed to stir for a day to ensure saturation adsorption. The *q* value was determined from UV/Vis data (supplementary data S10A). From the standard curve, the *q* was calculated. The *q* value of RGO@RS and GSC₇₅₀ was 60 and 50–55 mg/g of carbon content, respectively. The q of our material (GSC) is 75.4 mg/g in terms of carbon content. The q of AC for R6G reported in batch experiments is 44.7 mg/g [35] which is much lower than that observed for GSC. For CP, GSC exhibited a *q* of 52.6 mg/g of carbon under identical conditions (supplementary data Fig. S10B).

Fixed-bed experiments were also conducted to compare adsorption efficiency. Columns of equal diameter were taken and packed with adsorbents (GSC, GSC750, RGO@RS and sand) with equal bed height of 3 cm. Graphenic content in all the adsorbents were 0.5 wt%. R6G (1 ppm) was passed through the columns packed with the adsorbent at the flow rate of 2.3 mL/min. It was observed that while the sand got exhausted after passing 60 mL of R6G, whereas the other adsorbents had higher capacity. The column packed with GSC750 and RGO@RS showed 35 (2.1 L) and 48-fold (2.9 L) increase in q than regular sand. GSC showed the highest q among all the adsorbents, the column got exhausted after passing 3.6 L of R6G solution, which shows a 60-fold increase in *q* than sand itself. Recently, Gao et al. claimed a 5-fold higher *q* than regular sand for 'super sand' [20]. A comparison of different adsorbents is shown in Fig. 9. These results clearly indicate that our material is superior to other adsorbents in terms of q and it has about 12 times more adsorption efficacy compared to 'super sand' and can function as



Fig. 8. (A) Breakthrough curves showing the performance of the adsorbent composite in removing R6G from water for three consecutive adsorption cycles and (B) efficiency bar (initial R6G concentration = 1.0 mg/L; pH = 7 ± 0.2; bed depth = 3 cm; loading = 0.6 wt% (carbon content), particle size = 0.2 mm and flow rate = 2.3 mL/min). (B) The amount of R6G desorbed in three consecutive cycles of desorption using acetone as the eluent.



Fig. 9. Comparison of adsorption capacity with different graphenic adsorbents. Estimated error bar is 5%.

a cheaper and superior substitute. For want of a better word, we name this as 'wonder sand'.

4. Post-adsorption analysis of the adsorbent

The adsorbent was analyzed after the adsorption process to check the presence of the contaminants. Fig. 10A shows the SEM and EDAX characterization of GSC after the adsorption of chlorpyrifos. We can clearly see that the morphology of the GSC does not change during the adsorption process. However, EDAX identified signatures of P, S and Cl which was not present in the parent sample (data given earlier), which points to the presence of chlorpyrifos adsorbed on the particle. After regeneration, the sample was again analyzed using SEM and EDAX. The absence of P or Cl indicates the removal of chlorpyrifos (supplementary data S11).

In Fig. 10B, the LDI data confirms that the adsorption has taken place on the surface of GSC. There is no peak corresponding to GSC either in positive or negative mode (the data presented here is in positive mode, trace i). After the complete exhaustion of the adsorbent (R6G and CP adsorption in batch), the material was filtered and dried under N2 atmosphere. The sample was spotted on the LDI plate. The LDI MS in positive mode of the R6G sample (Fig. 10B (ii)) shows a peak at m/z 444 corresponding to $C_{28}H_{31}N_2O_3^+$ (R6G) and the fragmented peaks at m/z 415 and 386 due to the elimination of ethyl groups from the side chain. The LDI of GSC adsorbed CP was taken in negative mode, Fig. 10B (iii) showing fragmented peaks at m/z 181, 79 and 228 corresponding to C₅HCl₃N⁻, (SPO₂)⁻ and (C₅HCl₃NPO)⁻. The fragmented structures are shown in supplementary data of Fig. S12. The inset shows the isotopic distribution due the presence of three Cl groups at a mass difference of two (the peak at m/z 181 is enlarged). This categorically proved the adsorption of targeted pollutants on GSC.



Fig. 10. (A) SEM and EDAX characterization of adsorbent after adsorption of chlorpyrifos. (B) LDI of (i) GSC, (ii) R6G adsorbed on GSC and (iii) CP adsorbed on GSC. Inset shows an expanded view of the peak at *m*/*z* 181.



Fig. 11. (A) Raman spectrum of (i) R6G adsorbed on GSC and (ii) SERS of R6G. (B) Evaluation of the capacity of the column. SERS collected from the R6G spiked water sample after passing (i) 2 L, (ii) 3.6 L and (iii) 4.8 L through the column. The inset shows the photograph of (a) GSC, (b) R6G adsorbed GSC and (c) GSC after regeneration. (Inset of B is in color and this can be viewed in the Web version of the article.)

Unlike pesticides, the characteristic colors of the dyes can be used to identify the adsorption or desorption of these substances. The adsorption of R6G was evident from the color change (black to reddish) of the adsorbent particle (photograph in the inset of Fig. 11B). After regeneration, the adsorbent completely regained the initial color (black). Expanded photographs of the materials are presented in supplementary data S13 so that the color changes are appreciated.

However, trace amounts of R6G can be present on the adsorbent even without giving visual color. R6G being a Raman active molecule, Raman spectroscopy was employed for this analysis. Due to the inherent fluorescence of R6G, normal Raman spectrum was not able to show the characteristic features. In such cases, surface enhanced Raman spectroscopy (SERS) can be a useful technique to identify the sample. Hence, we used silver nanoparticles, which are known to be highly active SERS substrates [36,37]. We can see that the normal Raman spectrum does not have prominent features of R6G as in Fig. 11A (red trace) whereas the SERS spectrum obtained using silver nanoparticles showed all the characteristic features of R6G (Fig. 11A (black trace)). GSC before adsorption of R6G does not have the fluorescence background and the presence of this background (which masks other features) confirms the presence of R6G on GSC.

To assure complete regeneration of the adsorbent, the adsorbent was washed with acetone at a flow rate of 2.3 mL/min. The acetone extract after different wash cycles were analyzed. It was found that after 42 bed-volume of washing, no trace of R6G remained in the SERS spectra (supplementary data S14) pointing to the complete removal of R6G from the adsorbent surface. A similar strategy was used to calculate the capacity of the column. The bed height of the column was 3 cm (containing silica particle of size 0.3 µm and graphenic carbon loading of 0.6%). The filtrate was collected after different time (volume passed through the column) and was analyzed using SERS. Fig. 11B shows the SERS spectra taken from filtrate collected after passing 1 ppm of R6G solution through the column at different times (different volumes passed through the column). We can see that the evolution of peaks started after the passage of 3.6 L (1 ppm) of R6G solution through the column and appreciable features were seen when the volume passed through the column reached 4.8 L.

5. Conclusions

A facile in situ strategy for the synthesis of graphene-sand composite (GSC) is reported. A cheap and abundant material, asphalt was used as the carbon precursor. The synthetic strategy used here is useful to produce graphenic materials in solution phase as well as on solid substrates. The formation of graphenic materials was confirmed by different spectroscopic and microscopic techniques. Characteristic G and D bands were observed at 1578 cm⁻¹ and 1345 cm⁻¹, respectively, in the Raman spectrum. The 2D sheetlike structure with wrinkles observed in TEM and SEM confirmed the formation of graphenic materials. The as-synthesized composite, GSC, was tested for its applicability in decontaminating water. Rhodamine-6G and chlorpyrifos, a dye and a pesticide, respectively, were taken as the model pollutants. Batch experiments indicated that adsorption is highly dependent on the particle size, and carbon loading on sand particles. The suitability of the adsorbent in real time application was demonstrated through laboratory column experiments. The performance of GSC was compared to some other reported graphenic adsorbents and the results illustrated that GSC is superior in terms of strength and adsorption capacity for the contaminant tested. The adsorption capacity of GSC is 75.4 mg/g while it is 44.7 mg/g for AC in the case of R6G. The reusability of the adsorbent was demonstrated and found that the material is reusable and hence economically viable. The present study illustrates the possibility of making large quantity of graphenic materials in a cost effective manner and it is likely to be used in water purification industry.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jhazmat. 2012.12.022.

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